

AMENDED SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to Composite Metal-Polymer Compositions

5 We, NATIONAL LEAD COMPANY, a Corporation organised under the laws of the State of New Jersey, United States of America, of 111, Broadway, New York 6, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to composite metal-polymer compositions, and a process for their manufacture. Many procedures have been proposed heretofore for incorporating solid 15 particles, including metal particles, in polymeric materials with the object of modifying or altering the properties of the polymeric materials, such as to incorporate materials opaque to certain types of radiation, or to 20 make the solid particles more readily dispersed in organic paint vehicles for incorporating metallic pigments into paint.

25 One method of producing a dispersion of the desired material in the polymer is to prepare the desired polymer, then melt the polymer by heating, and then stir in the desired material. This method, however, resulted in poor dispersion of the material in the polymer and entailed the exposure of the polymer to the deleterious effects of prolonged heating. 30 Also, this method was completely inapplicable to the production of dispersions of the desired material in high-temperature flowing or non-flowing polymers, that is to say, those polymers with a melt index of less than about 0.7 as determined by the A.S.T.M. Test D-1238-52T. High-temperature flowing polymers are 35 subject to degradation upon milling at the

lowest practicable milling temperature. The temperature at which the degradation takes place varies with the particular polymer used. In the case of non-flowing polymers, the polymer would decompose upon an attempted milling. The temperature at which this decomposition takes place varies with the particular polymer used. 40 45

Another method of producing a dispersion of the desired material in the polymer is to dissolve the polymer in a suitable solvent and then precipitate the polymer in the presence of the desired material. This method, however, was limited to polymers which were readily soluble, and even when such readily soluble polymers were used, the resultant dispersion was a poor one, and was not at all uniform. 50 55

For shielding materials such as a polyethylene-lead mixture, a uniform dispersion of the lead in the polyethylene is highly desirable. Lead is effective as a shield against gamma rays, while polyethylene is effective as a shield against slow neutrons. Where the dispersion of lead in the polyethylene is not uniform, gamma rays are able to pass through the shield via transparent passages for gamma radiation left in the shield due to the poor dispersion of the lead in the polyethylene. 60 65

An object of this invention, therefore, is to provide an improved metal-polymer composition in which the metal is partly or wholly encapsulated by the polymer and a process for its manufacture. 70

Another object is to provide a metal-polymer composition in easily millable polymers and also in a high-temperature flowing or non-flowing polymer characterized by im- 75

proved dispersion of the metal in the polymer.

According to the present invention there is provided a composition comprising a metal, including boron, partly or wholly encapsulated by a polymer formed by polymerization of an aliphatic olefinically unsaturated polymerizable hydrocarbon *in situ* on the surface of the metal.

The present invention also provides a process for producing a metal-polymer composition, which process comprises treating a substrate of a metal, a mixture of metals or an alloy of metals of Group IB, II, III, IV, VB, VIB, VII or VIII of the Periodic Table with the components of a multi-component catalyst system comprising a reactive compound of a metal of Group IVB, VB, VIB, VIIB or VIII of the Periodic Table and an organometallic compound of a metal from Group IA, IIA, IIB or IIIA of the Periodic Table as hereinbefore defined, and further treating the thus treated metal substrate with an aliphatic olefinically unsaturated polymerizable hydrocarbon containing less than 6 carbon atoms comprising ethylene, propylene, butadiene or isoprene.

The Periodic Table referred to herein is the Periodic Chart of Elements from Fundamental Chemistry, 2nd Edition, by H. G. Deming, Wiley & Sons Inc., New York.

The substrates to which this invention is applicable include the metals of Groups IB, II, III, IV, VB, VIB, VII and VIII of the Periodic Table, mixtures of two or more of these metals or alloys of two or more of these metals. Exemplary of such metals are copper, magnesium, barium, mercury, boron, aluminium, yttrium, titanium, germanium, lead, tin, vanadium, chromium, molybdenum, manganese, iron, cobalt and nickel.

Even in the case of mercury, the mercury is so well dispersed in the polymer that it is entrapped within the polymer mass, and the resultant product consists of globules of mercury encapsulated by the polymer.

In general, the catalytic systems used in this invention may be those formed by mixing a reactive compound of a metal of Group IVB, VB, VIB, VIIB or VIII of the Periodic Table with an organo-metallic compound of a metal of Groups IA, IIA, IIB or IIIA of the Periodic Table. Such catalytic systems are well known and described in many places in the literature.

A reactive inorganic or organic salt, ester or complex of the metals of Group IVB, VB, VIB, VIIB or VIII, and especially the halides, oxyhalides and esters thereof, may be used. Thus a compound of titanium, zirconium, hafnium, thorium, vanadium, tantalum, chromium, molybdenum, tungsten, uranium, manganese, rhenium, iron or cobalt may be used. Exemplary of such compounds are zirconium tetrachloride, titanium tetrachloride,

titanium trichloride, vanadium dichloride, vanadium oxychloride, vanadium trifluoride, vanadium trichloride, vanadium oxydichloride, tantalum pentachloride, molybdenum trichloride, molybdenum pentachloride, chromium trichloride, chromium difluoride, ferric chloride, manganese dichloride, vanadium oxyacetylacetonate, iron acetylacetonate, cobalt acetylacetonate, chromium acetylacetonate, manganese acetylacetonate, alkyl vanadates and alkyl titanates. Instead of adding the components of the catalytic system separately the components may be mixed together before addition to the metal particles. In this procedure the catalytic system may comprise, for example, a compound such as titanium tetrachloride or vanadium tetrachloride and an organometallic compound of an alkali metal, alkaline earth metal, zinc or aluminium.

Any organometallic compound of a metal of Groups IA, IIA, IIB and IIIA of the Periodic Table, e.g., an alkali metal, alkaline earth metal, zinc or aluminium, may be used. Exemplary of such organometallic compounds are the alkali metal alkyls or aryls such as butyl-lithium, amylsodium and phenylsodium, dimethylmagnesium, diethylmagnesium, diethylzinc, methylmagnesium bromide, butylmagnesium bromide, phenylmagnesium chloride, trimethylaluminium, triisobutylaluminium, trioctylaluminium, tridodecylaluminium, dimethylaluminium bromide, diethylaluminium chloride, ethylaluminium dibromide, isobutylaluminium sesquichloride, dipropylaluminium iodide, diisobutylaluminium fluoride, diisobutylaluminium bromide, diethylaluminium hydride, ethylaluminium hydride and diisobutylaluminium hydride, and complexes of such organometallic compounds, as for example, sodium aluminium tetrabutyl, lithium aluminium tetraoctyl and sodium aluminium triethylchloride.

The molar ratio of the organometallic compound to the transition metal compound in carrying out the reaction may be varied over a wide range, but usually there should be present 1 to 4 moles of reactive alkyl or aryl groups of the organometallic compound for each mole of the transition metal of the transition metal compound.

It is usually preferable to utilize the transition metal compound in a soluble form, but in certain cases, such as zirconium tetrachloride, the compound may be used in a finely divided insoluble form.

As previously pointed out, organometallic compounds of metals of Group IA, IIA, IIB or IIIA of the Periodic Table, e.g., an alkali metal, alkaline earth metal, zinc or aluminium, are used in combination with the transition metal compound to act as a catalytic system in accordance with this invention. Thus alkali metal alkyls or aryls, alkaline

earth metal alkyls or aryls, aluminium alkyls, metal alkyl halide or hydride may be used.

The catalytic systems described above when used in the process of this invention, yield a metal-polymer composition wherein the polymer is characterized by its high density and high degree of crystallinity. In the case of polyethylene, this degree of crystallinity is 70% to 96%.

The selection of the temperature and pressure used for the process of this invention will obviously depend upon the activity of the catalytic system being used, the diluent used and the degree of polymerization desired. In general, the polymerization will be carried out at slightly elevated temperatures, but any temperature from -20°C. to 150°C. , and preferably from 30°C. to 100°C. , may be used. In the same way, while atmospheric pressure or a pressure of only a few pounds per square inch may be used, the polymerization may be carried out under a wide range of pressure, as for example, from a partial vacuum to about 2,000 pounds and preferably from atmospheric to 500 pounds per square inch pressure. Higher pressures may, of course, be used, but generally do not appreciably alter the course of the process.

The amount of polymer deposited on the metal may vary widely from almost no polymer to as much polymer as is desired to be used in conjunction with metal, depending on the end use intended for the product.

The metal-polymer compositions of this invention are not simple mechanical mixtures, as the metal is found to be tenaciously held by the polymer. Microscopic examination reveals the embedment of the metal particles within a matrix of the polymer.

The mechanism by which the compositions of this invention are formed is not fully established. It is possible that the polymer is gummy or in a soft plastic state in the early stages of growth, and that it is this gumminess or plasticity which causes the polymer to adhere tenaciously to the metal. It is also possible that a reaction takes place between the catalyst and the metal surface or the oxide on the metal surface, and that the resultant material is a metal-catalyst composition on which the polymer grows, thus encapsulating the metal. Yet another possibility is that the transition metal is reduced to a less soluble form, which is deposited on and adheres to the metal surface, i.e., in the case of titanium, for example, the titanium in the tetravalent state is reduced to insoluble titanium compounds wherein the titanium is in a trivalent or divalent state, and that these insoluble compounds of trivalent and divalent titanium adhere to the substrate metal surface to form a metal-catalyst composition. The polymer may then grow on this metal-catalyst composition and encapsulate the metal. The process of encapsulation is aided by a suitable

reaction medium, selected so that this medium is a poor solvent for the polymer in question. Thus, heptane or toluene are suitable for the deposition of polyethylene.

The monomers useful in this invention include ethylene, propylene, butadiene and isoprene.

The dispersion of the metal in the polymer is much more complete, and the metal is more completely embedded in the polymer than can be achieved by ordinary physical means.

Using the process of this invention, we are able to obtain a complete dispersion of the metal in high-temperature flowing or non-flowing polymers.

In using the process of this invention, no further steps after the polymerization process is complete are needed, other than moulding, to produce a useful commercial article. As to moulding, the compositions of this invention may be moulded either under pressure at room temperature, or under pressure at elevated temperature. Room temperature moulding results in a considerable saving to the user of such moulding powder, as heat need not be generated in order to accomplish a successful moulding.

Following is a description by way of example of methods of carrying the present invention into effect.

EXAMPLE I

Powdered lead, 45 grams, was dispersed in 500 ml. of toluene and the entire mixture was sparged with nitrogen. Titanium tetrachloride, 0.02 mole, was added and the reaction mixture was then agitated for $\frac{1}{2}$ hour. Methylmagnesium bromide, 0.045 mole, was added to the reaction mixture and the passage of ethylene into the reaction mixture was commenced. The reaction mixture was heated to 50°C. and maintained there until the desired amount, 45 grams, of ethylene had been passed in, as measured by a flow meter. The flow of ethylene was then halted, and the reaction terminated. The product was filtered off and washed repeatedly with methanol. The resultant material contained approximately 50% lead and 50% polyethylene by total weight of the lead plus polyethylene.

EXAMPLE II

The procedure of Example I was repeated several times except that the lead was replaced each time by an equivalent amount by weight of one of the following powdered metals: copper, barium, iron, aluminium, nickel, titanium, tin, chromium, manganese, cobalt and vanadium. Each time, the resultant product contained approximately 50% metal and 50% polyethylene by total weight of the metal plus polyethylene.

EXAMPLE III

The procedure of Example I was repeated, except that 20 grams of propylene were used instead of ethylene and the reaction was run under 100 pounds per square inch pressure.

The amount of propylene used was determined by using two flow meters, one to measure the amount of propylene passed into the reaction mixture and the other to measure the amount of propylene passing out. The amount of powdered lead used was 85 grams. The catalytic system used comprised 0.01 mole of titanium trichloride and 0.002 mole of triethylaluminum. The resultant product contained approximately 90% lead and 10% polypropylene by total weight of the lead plus polypropylene.

EXAMPLE IV

The procedure of Example III was repeated, except that 1,3-butadiene was used instead of propylene. The amount of lead used was 45 grams. The amount of 1,3-butadiene in the reaction mixture was 5 grams. The catalytic system used comprised 0.006 mole of vanadium trichloride and 0.003 mole of diethylzinc. The resultant product contained approximately 95% lead and 5% polybutadiene by total weight of the lead plus the polybutadiene.

EXAMPLE V

The procedure of Example I was repeated, except that 10 grams of isoprene were used. No flow meter was used. The catalytic system used comprised 0.0013 mole of vanadium trichloride and 0.04 mole of triethylaluminum. The amount of lead used was 50 grams. The resultant product contained approximately 85% lead and 15% polyisoprene by total weight of the lead plus the polyisoprene.

EXAMPLE VI

The procedure of Example I was repeated, except that 5 grams of ethylene were used. The resultant product contained approximately 90% lead and 10% polyethylene by total weight of the lead plus polyethylene.

EXAMPLE VII

The procedure of Example I was repeated except that 102 grams of boron and 110 grams of ethylene were used, and the catalyst was 0.0158 mole of titanium tetrachloride and 0.0158 mole of triethylaluminum. The boron, because of its pyrophoric character, required special handling under a nitrogen atmosphere at all times. The reaction mixture was heated to 60° C. and maintained there until the desired amount of ethylene, 110 grams, had been passed into the reaction mixture. The flow of ethylene was then halted, and the reaction terminated. The product was filtered off and washed repeatedly with methanol. The resultant material contained approximately 63% polyethylene and 37% boron by total weight of the boron plus the polyethylene. In addition, it was found that the boron, when encapsulated, had lost its pyrophoric character, did not react with water and did not react with methanol.

EXAMPLE VIII

The procedure of Example VII was repeated except that 102 grams of magnesium

powder was used instead of the boron. Because of the pyrophoric quality of the magnesium powder, the same precautions used were taken as in Example VII. The resultant product contained approximately 48% polyethylene and 52% magnesium, based on the total weight of the magnesium plus polyethylene.

EXAMPLE IX

The procedure of Example I was repeated except that 110 grams of ethylene were used and the catalyst was 0.0158 mole of titanium tetrachloride and 0.0158 mole of triethylaluminum. The metal used was 102 grams of mercury, and a high-speed disperser was used in the reaction mixture. The reaction temperature was maintained at 60° C. while the ethylene was being passed in and until the reaction was complete. The resultant material contained approximately 25% mercury and 75% polyethylene based on the total weight of mercury plus polyethylene. The resultant product had a greyish cast to it. This greyish colour is due to the presence of the mercury in the composition, which can be seen microscopically as a fine dispersion of the metal in the larger polyethylene particles.

The lead-polyethylene composition may be used for shielding, by virtue of the absorption of gamma rays by the lead and slow neutrons by the polyethylene. The lead-polyethylene compositions may be varied, as regards the proportion of lead to polyethylene, to suit the individual requirements of the user of such shielding. In addition, the lead-polyethylene composition of this invention may also be used to fabricate gloves and laboratory aprons for use in radiation shielding.

Protection from alpha particles is a relatively simple matter. Rubber gloves, for example, are sufficient to absorb the alpha particles. Protection against beta radiation is also a relatively simple matter. The thickness of the required shielding for beta particles of a given energy decreases with increasing density of the material. The use of a heavy metal, which implies an element of high atomic number, however, is not advisable because the production of braking radiation accompanying the deceleration of the beta particles in the absorber tends to increase with atomic number. For this reason therefore it is preferable to use materials of low atomic weight for shielding from beta particles. Aluminium is satisfactory for many purposes. Thus, as regards an aluminium-polyethylene composition, the aluminium would protect against beta particles and the polyethylene would stop the slow neutrons. Thus, a mixture of aluminium and lead may be encapsulated in polyethylene, and when such a material is used for shielding it would yield protection against beta particles, gamma rays and slow neutrons.

On account of their considerable penetrat-

ing power, the absorption of neutrons and gamma rays is a much more difficult matter. Both of these radiations are extensively produced in nuclear reactors, the former being liberated in the fission process, whereas the latter are emitted by the fission products. It is the intense gamma activity of the latter which makes it necessary to handle spent fuel elements by remote control. As with beta rays, the best absorbers for gamma radiation are materials of high density. In this case, however, high atomic number is an advantage, and hence lead, which has both a high density and a high atomic number, has been accepted as one of the best materials for gamma shielding.

As regards iron and barium, these elements of high mass number slow down the very fast neutrons by inelastic scattering collisions, and also help greatly in the attenuation of the gamma radiation. Boron has been found to absorb slow neutrons, but it will not protect against gamma rays.

Thus, from the above description, it is readily apparent that a wide variety of metal-polymer compositions consisting of one or more metals, depending on the shielding use it is intended for, may be prepared and used effectively.

The metal-polymer compositions of this invention may be used generally as moulding powders to produce a wide variety of moulded articles and the polymer of this composition provides an important self-lubricating action. The moulding can be readily accomplished at room temperature or elevated temperature under pressure, the polymer forming the moulding matrix for the metal. In addition, the metal of such a moulding powder is protected against the formation of oxides and against the action of moisture in the air by virtue of the metal being encapsulated by the polymer. In the case of boron, for example, the boron is completely protected against the action of water, and against the action of other materials such as methanol. All metals, particularly those which are active in a finely divided form, such as nickel and magnesium, are protected against the deleterious action of other materials, and of atmospheric conditions. In this way, metals may be stored indefinitely without the necessity for protective measures to guard against both the deleterious action of atmospheric conditions beyond the control of the consumer of the metals, and the deleterious action of chemicals which might have ordinarily come in contact with the metal, particularly where the metal powder is pyrophoric.

The metal-polymer compositions of this invention may be used in a new type of powder metallurgy. Metal-polymer compositions extremely rich in the metal may be prepared and moulded into a wide variety of articles; and such a moulded article would not

be held together by the conventional metal to metal bond of the usual powder metallurgical composition, but rather, they would be held together by a polymer matrix, thus requiring simpler moulding conditions than in conventional powder metallurgy.

In the case of a mercury-polymer composition, such a composition renders the mercury amenable to uses such as mildewcides and to protect ships' hulls from the formation of barnacles and the attack of other marine life. Also, the fact that the mercury is encapsulated in the polymer, protects the mercury and prevents the formation of any oxide of mercury.

In addition, it is thought that the boron-polymer compositions of this invention may possibly be used in jet fuel compositions. The polymer itself is readily ignitable and would add to the usefulness of boron in jet fuel compositions. In addition to its other uses, boron's ability to absorb neutrons may add to its utility as a shielding material.

Iron-polymer, nickel-polymer and cobalt-polymer compositions have been found useful as non-conducting magnets in addition to their other uses.

In addition, the aforementioned metal-polymer compositions may be moulded into various shapes, and these moulded articles may be magnetized if desired.

WHAT WE CLAIM IS:—

1. A composition comprising a metal, including boron, partly or wholly encapsulated by a polymer formed by polymerization of an aliphatic olefinically unsaturated polymerizable hydrocarbon *in situ* on the surface of the metal.
2. A composition as claimed in claim 1, wherein the metal is finely divided.
3. A composition as claimed in claim 1 or claim 2, wherein the metal is a metal of Groups IB, II, III, IV, VB, VIB, VII or VIII of the Periodic Table as hereinbefore defined.
4. A composition as claimed in claim 1 or claim 2, wherein the metal is lead.
5. A composition as claimed in claim 1 or claim 2, wherein the metal is aluminium.
6. A composition as claimed in claim 1 or claim 2, wherein the metal is iron.
7. A composition as claimed in claim 1 or claim 2, wherein the metal is boron.
8. A composition as claimed in claim 1 or claim 2, wherein the metal is magnesium.
9. A composition as claimed in any one of the preceding claims, wherein the polymer is polyethylene, polypropylene, polybutadiene or polyisoprene.
10. A composition as claimed in any one of the preceding claims, wherein the polymer is a high-temperature flowing polymer as herein defined or a non-flowing polymer.
11. A composition as claimed in any one of claims 1 to 9, wherein the polymer is

polyethylene having a degree of crystallinity of from 70% to 96%.

12. A composition as claimed in claim 1 or claim 2, wherein the metal is lead and the polymer is polyethylene.

13. A process for producing a metal-polymer composition, which process comprises treating a substrate of a metal, a mixture of metals or an alloy of metals of Group IB, II, III, IV, VB, VIB, VII or VIII of the Periodic Table with the components of a multicomponent catalyst system comprising a reactive compound of a metal of Group IVB, VB, VIB, VIIB or VIII of the Periodic Table and an organometallic compound of a metal from Group IA, IIA, IIB or IIIA of the Periodic Table as hereinbefore defined, and further treating the thus treated metal substrate with an aliphatic olefinically unsaturated polymerizable hydrocarbon containing less than 6 carbon atoms comprising ethylene, propylene, butadiene or isoprene.

14. A process as claimed in claim 13, wherein the catalytic system comprises titanium tetrachloride and methylmagnesium

bromide.

15. A process as claimed in claim 13, wherein the catalytic system comprises zirconium tetrachloride and methylmagnesium bromide.

16. A process as claimed in claim 13, wherein the catalytic system comprises titanium tetrachloride and a trialkylaluminium.

17. A process as claimed in claim 13, wherein the catalytic system comprises titanium tetrachloride and triethylaluminium.

18. A process as claimed in claim 13, wherein the catalytic system comprises titanium tetrachloride and triisobutylaluminium.

19. A process for producing a composition as claimed in any one of claims 1 to 12 substantially as described with reference to any one of the specific Examples hereinbefore set forth.

20. A composition when produced by a process as claimed in any one of claims 13 to 19.

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